

EXPERIMENTS IN DIAMOND FILM FABRICATION IN TABLE-TOP PLASMA APPARATUS

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KEY WORDS: Diamonds, plasma, heterojunctions, photoconductors.

PREREQUISITE KNOWLEDGE: The student should be familiar with the basics of materials science and chemistry. Levels at which these experiments are performed are second semester junior and either semester senior year. The students are first given lectures on band structure in solids, film formation via chemical vapor deposition, semiconductor junction formation, and photoconductivity. Though a scanning electron microscope would be helpful, film morphology can be seen with reasonable optical microscopy. A video filmed by the instructor showing the plasma deposition onto silicon and sapphire gives the student an idea of what is expected.

OBJECTIVES: To illustrate the process of plasma assisted chemical vapor deposition and to show devices which can be made simply in the laboratory. These devices illustrate clearly the concepts of bandgap, junctions, and photoelectronic processes. Films and devices are measured electrically, optically, and thermally.

EQUIPMENT AND SUPPLIES:

- (1) Silicon wafers, sapphire wafers, and microscope slides (one per student)
- (2) U.S.P. ethyl alcohol
- (3) Stoppered flask with tubing fittings
- (4) Controlled air leak
- (5) High voltage (>2000 volts) d.c. supply
- (6) Microwave oven (500 watts), small (optional)
- (7) Polycarbonate belljar (25 cm. diameter)
- (8) Silver paint (DuPont 4817)
- (9) Diode curve tracer
- (10) Microscope (optical, 400x) or electron microscope

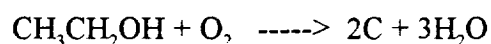
INTRODUCTION: Using simple chemicals and materials, such as ethyl alcohol, sapphire, and silicon wafers, students can heteroepitaxially deposit diamond films onto silicon and sapphire wafers in a direct current plasma and/or microwave assisted plasma. By placing 1 part in 10^6 of either boron trichloride or phosphorus trichloride into the ethyl alcohol, the diamond films can be doped p- or n-type respectively. Undoped films serve as good photoconductor films. Small polycarbonate belljars purchased from Cole-Parmer along with mini vacuum pumps serve as the reaction chamber, minimizing danger of accident. The systems may be placed into a small microwave oven (500 watts, 2.45 GHz). The reaction with partial pressures of oxygen combined with the ethyl alcohol yields diamond films whose properties are dependent on deposition variables heretofore unknown to the student (and sometimes to the professor).

The three laboratory sessions spent provide the student with experience in:

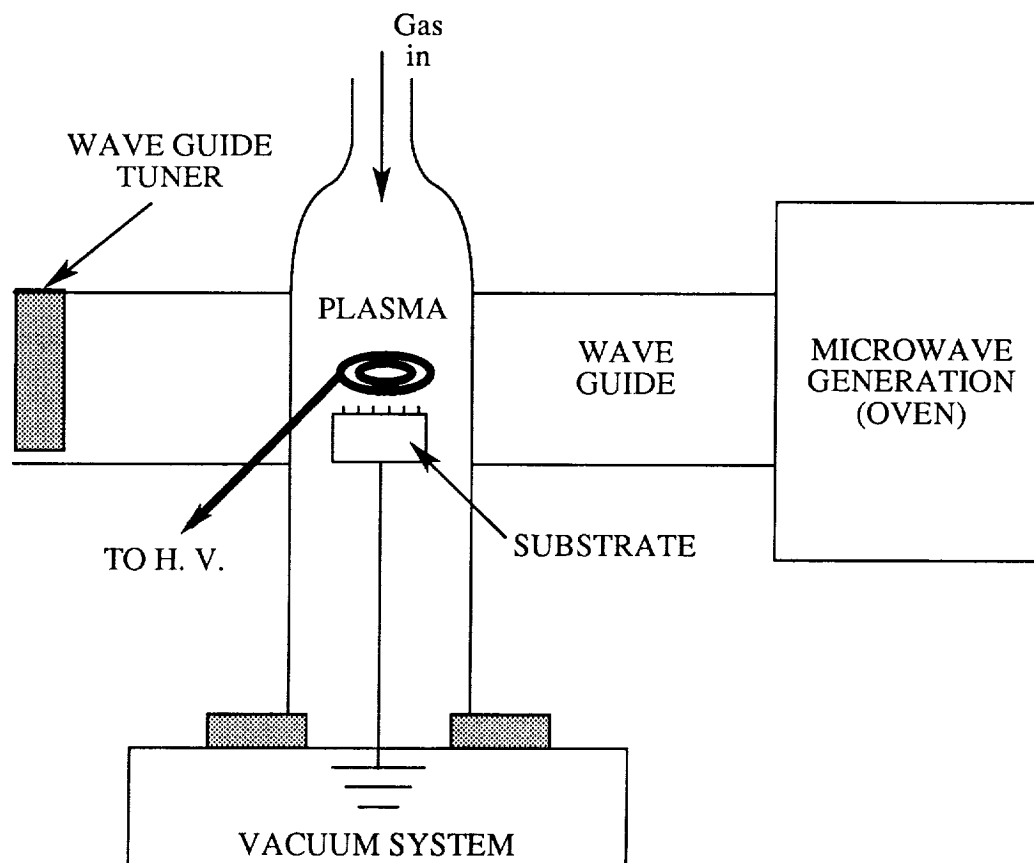
1. Chemical vapor deposition;
2. Plasma assisted reactions;
3. Heterojunctions and band structures;
4. Photoconductivity and spectrophotometric identification of films; and
5. Microscopy of films.

These experiments were developed by the professor and seniors in the process of the senior design project capstone course at Western New England College.

The Reaction: Although the literature is replete with carbon sources made up of a carbon gas source (such as methane in argon), little is said regarding safer methods of laboratory use for students. For the sake of safety, availability, and cost, alcohols were chosen as sources. A typical reaction for the ethyl alcohol used is shown below.



System Design/Procedure: The apparatus shown in Figure 1 was the functional system used, with a modification of high voltage plasma assist. This system is a modification of that described by R. C. DeVries. The microwave source was a conventional 2.45GHz, 500 watt Toshiba microwave oven. The chamber was a polycarbonate belljar, supplied by Cole-Parmer. The substrates were not heated from an external source, since, in the presence of the microwave oven ground, arcing occurred.



The vacuum pump is run until the system reaches 80 microns or lower pressure. The pump is allowed to run while a mixture of 1 part air and 1 part argon is bubbled through the ethyl alcohol and "leaked" into the vacuum system until the pressure rises to 3-30 Torr. The microwave power and/or the high voltage was turned on and the plasma (blue-red column) decomposition/oxidation of the ethyl alcohol proceeded. It should be noted that the morphology of the films obtained was quite different, dependent on the plasma source used. Though the process works better with the semiconductive substrates, with microwave assist the sapphire and glass substrates also provide suitable substrates. All films are polycrystalline with reasonable densities; best results and densities were obtained on single crystal silicon substrates. Typical yellowing or browning of the film indicates the presence of carbon (or graphite) included in the film. Each system appears to have somewhat different characteristics and the experimenter should note these. Typical growth rates of these films are of the order of 0.01 to 0.1 micrometer per minute. An x-ray diffraction scan of a film on (100) Silicon is shown in Figure 2. This film was grown at approximately 0.06 micrometers per minute.

Typical dopants for the diamond film are introduced via dissolution of boron trichloride (acceptor) and ammonium chloride (donor) into the ethyl alcohol in the 1-100 ppm ratio to carbon in the alcohol. Care should be taken to clean the system well between each type change. The number of ionized acceptors and donors is only expected to be from 1-10% in the diamond film at room temperature. Though time usually doesn't permit, all four varieties of n/p, p/n, n/n, and p/p heterojunctions prove to be interesting in demonstrating isotype and heterotype heterojunctions and their characteristics.

Safety Note: Although the alcohol is safer than methane in the laboratory, a safety mesh or Plexiglas sheet should be placed between the student and the apparatus. Good practice indicates the wearing of safety masks during the deposition.

Device Preparation: Devices of the heterojunction type are post-deposition prepared by roughing the back side of the silicon wafer with 00 grit silicon carbide paper. Silver paint (DuPont #4817) is applied to the back of the silicon wafer and is allowed 15 minutes to dry. Dots of silver paint may be applied to the front of the wafer over the diamond. Fine aluminum wires may be attached for testing of the devices. Sufficient light enters the device to cause both photovoltaic and photoconductive (reversed biased) responses in the junctions. Devices of the non-junction photoconductive types on either sapphire or glass work well with silver paint electrodes applied juxtaposed in parallel bar formation. Both devices are shown in Figure 3. Carbon or gold semi-transparent electrodes function better for photo devices and can be easily deposited as replacements for the silver on diamond top electrodes. Attachment to these electrodes by means of fine aluminum wires serves to ease testing of the devices in the absence of probes.

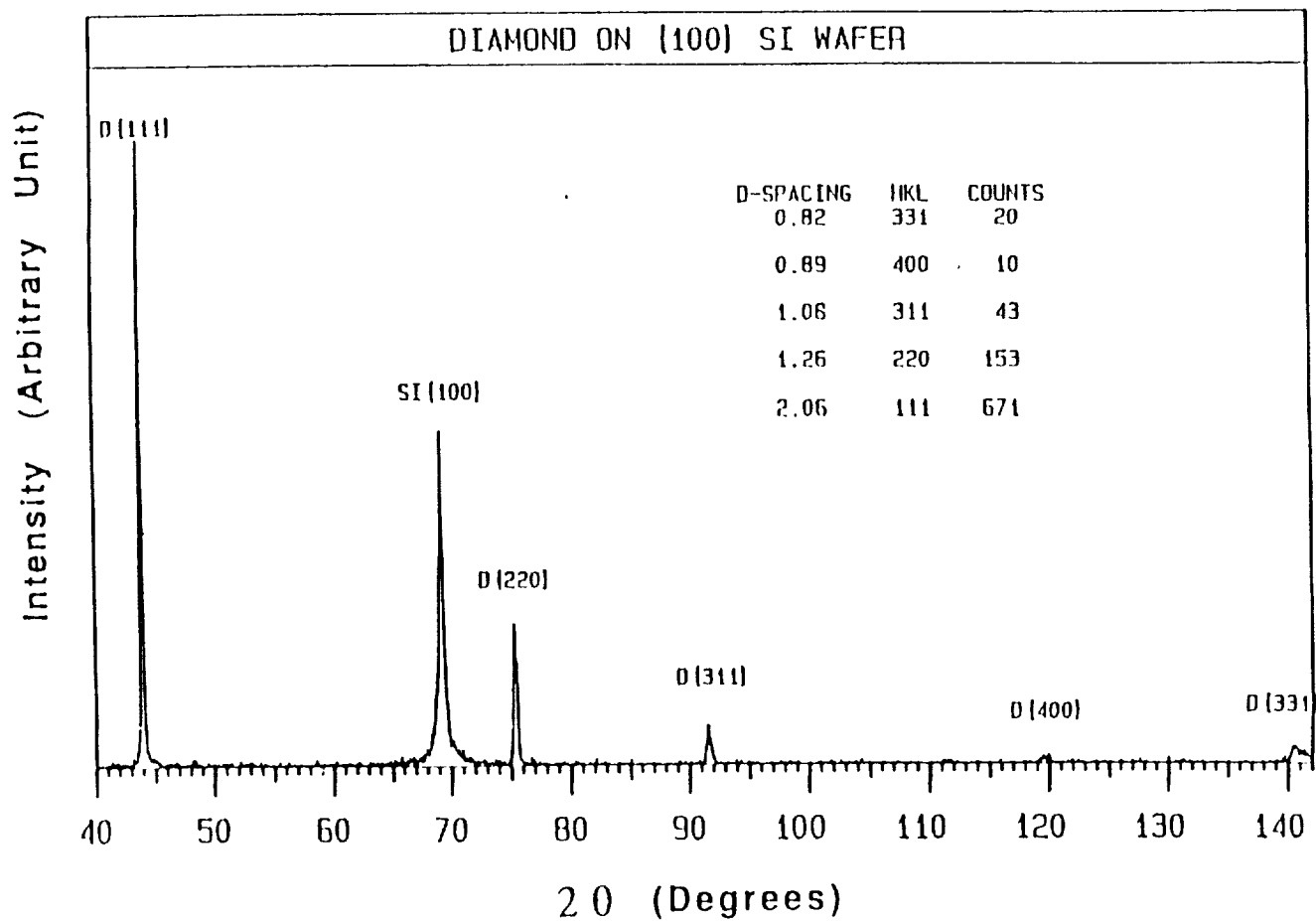
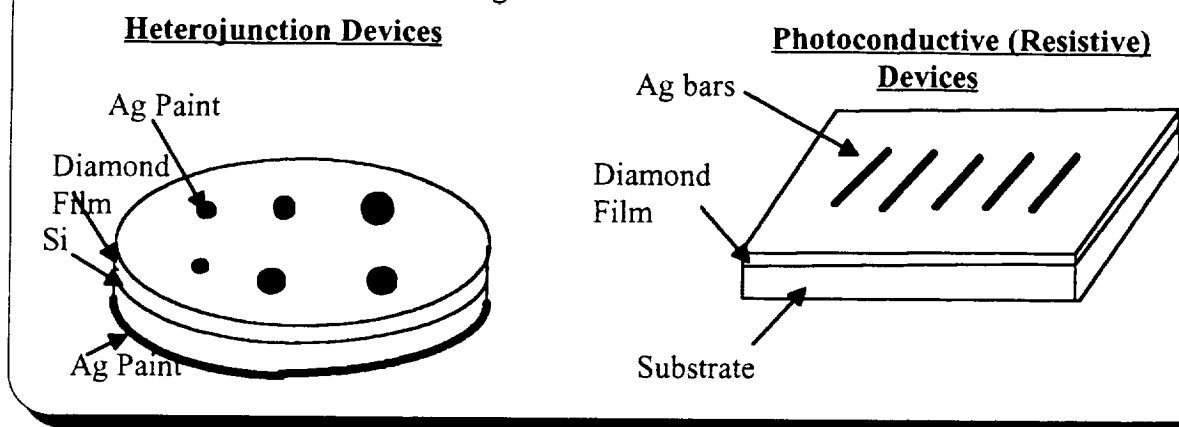


Figure 2
X-ray Diffraction of Diamond Film on Silicon (100)

Figure 3



Typical Measurements: Measurements made on devices will vary according to doping levels, type mixes, resistivities of the silicon, and conditions of deposition. Typical diode characteristics in the dark and light are shown in Figures 4 and 5. Typical photoconductor characteristics are shown for light and dark conditions in Figures 6 and 7. All characteristics are taken on a Tektronix curve tracer. The light sources used were tungsten-halogen "white" and 253.7 nm ultraviolet.

A typical spectrophotometric transmission curve vs wavelength for diamond is shown in Figure 8. The cutoff (bandgap) wavelength as well as impurity and other absorption energy levels are easily calculated (as shown in the appendix) from

$$E = hc/\lambda.$$

Spectral response characteristics can optionally be made with an added expenditure of time and effort.

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SOURCES OF SUPPLY: The microwave oven was an \$88 one obtained from a local appliance store. The laboratory supplies and chemicals were obtained from Cole-Parmer and Fisher Scientific. The high voltage supply is a \$35 surplus TV. 4000 volt d.c. supply. The silicon wafers and sapphire disks were obtained through Ms. Shannon John, Wafernet, San Jose, CA. The silver paint was obtained from Bert Bricker, Wilmington, DE. All other supplies are easily obtained from local university supply houses.

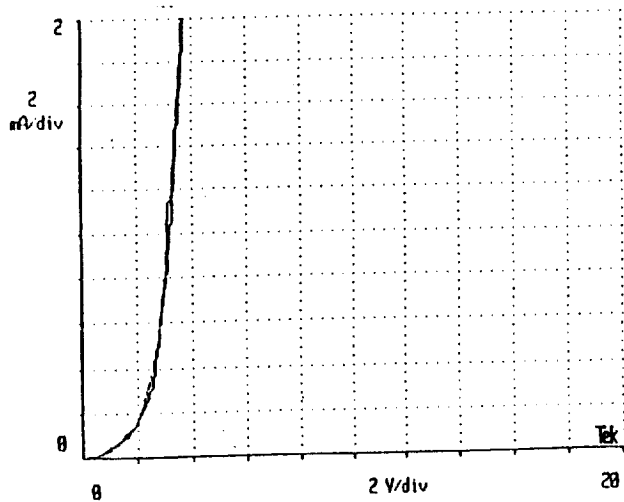


Figure 4

Forward Biased p/n Diamond/Si Heterojunction Diode

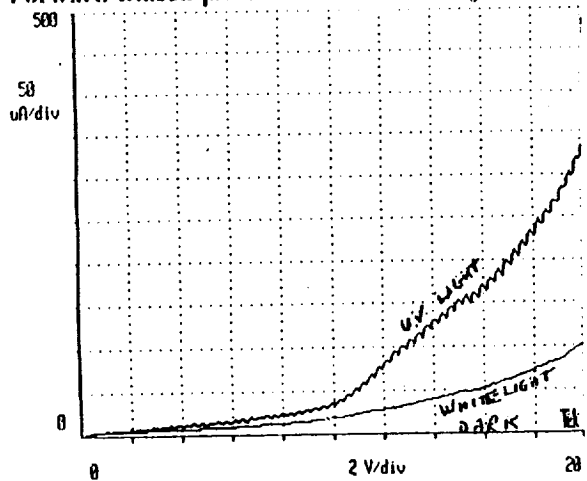


Figure 6

Low Sensitivity Diamond Photoconductor on Glass

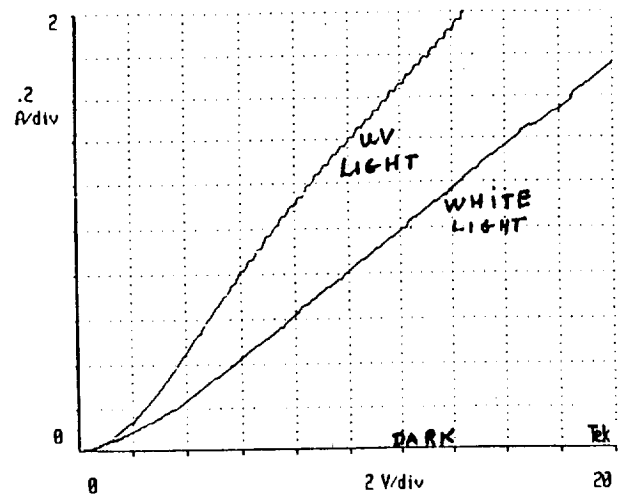


Figure 5

Reverse Biased p/n Diamond/Si Heterojunction Diode

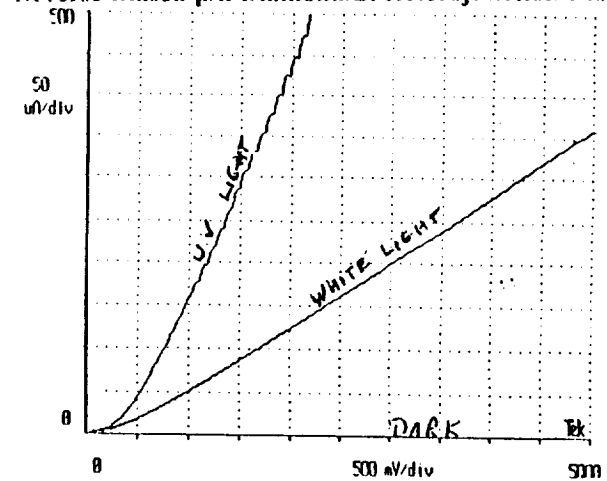
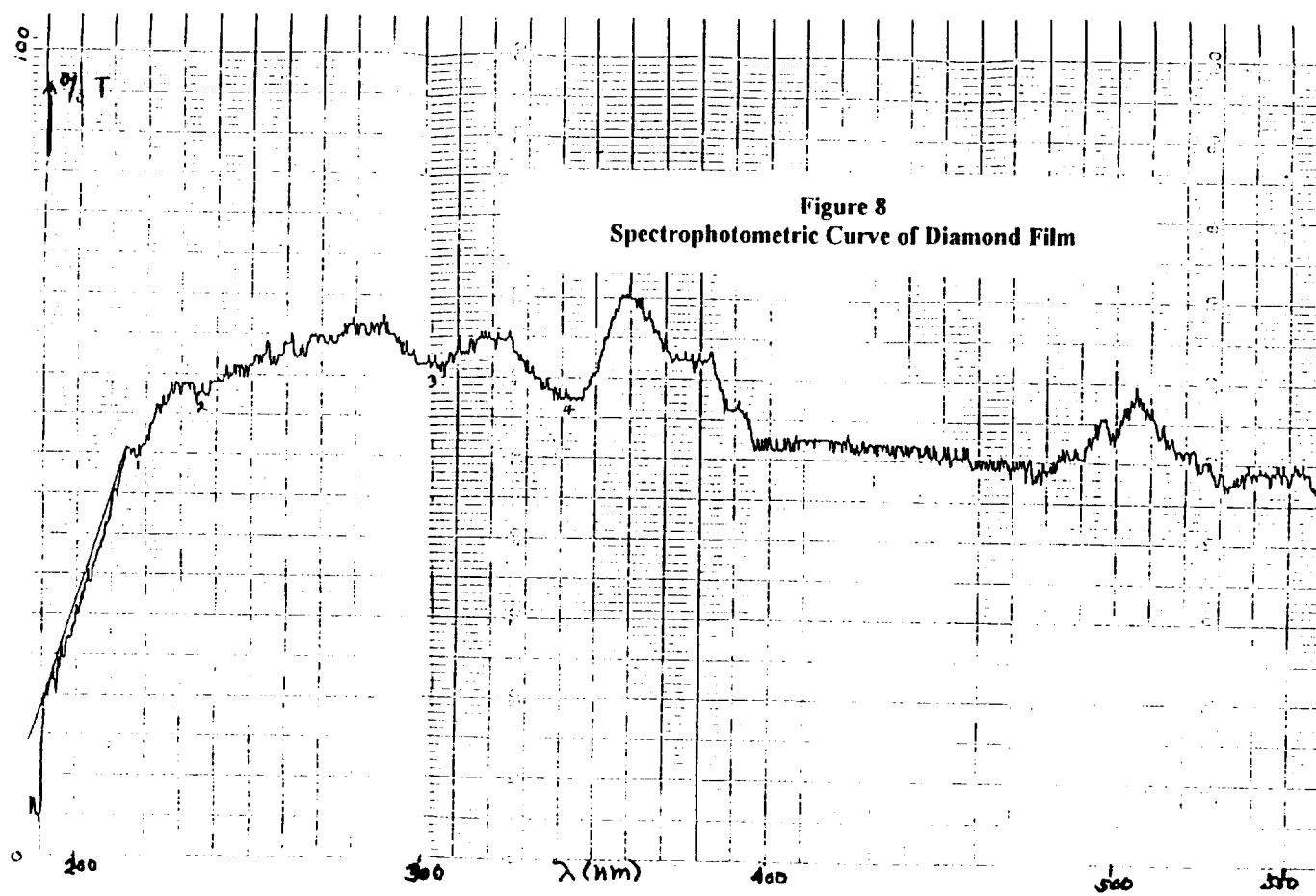


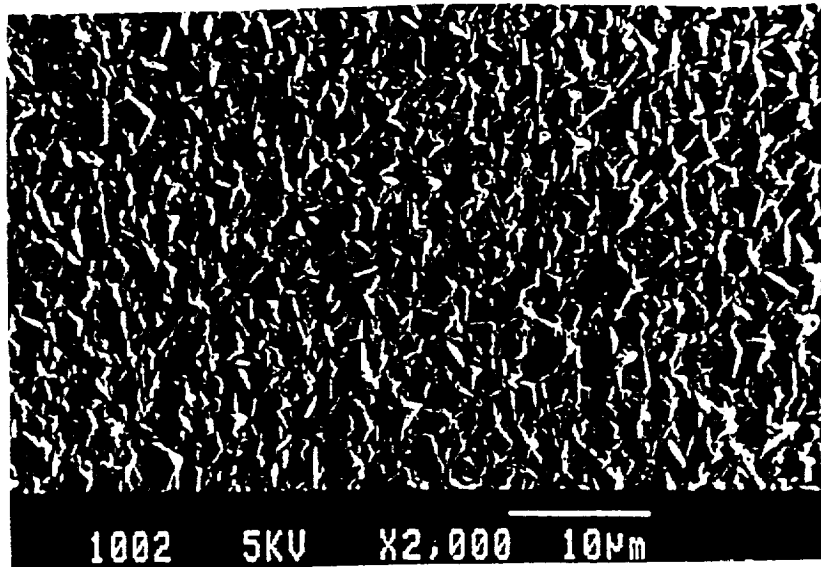
Figure 7

High Sensitivity Diamond Photoconductor on Sapphire

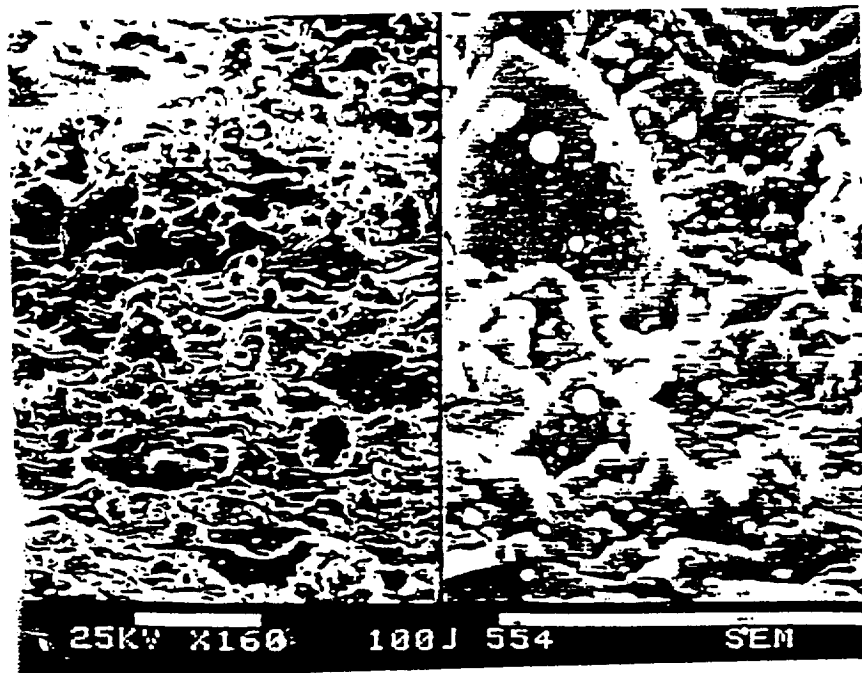


Some original figures were unavailable at time of publication.

APPENDIX



Diamond Film #3



Diamond Film at 160x and 320x Magnification and 30° Angle

APPENDIX:

Heterojunction Theory: Heterojunctions are semiconductor junctions which are composed of two or more materials of differing band gaps in metallurgical contact with one another. The Anderson Model (in the reference by Milnes and Feucht) was the model chosen for diamond on silicon, n/n, p/p, p/n, and n/p structures. The energy band diagram for isolated and in-contact n/p (Si/diamond) is shown in Figures A1 and A2.

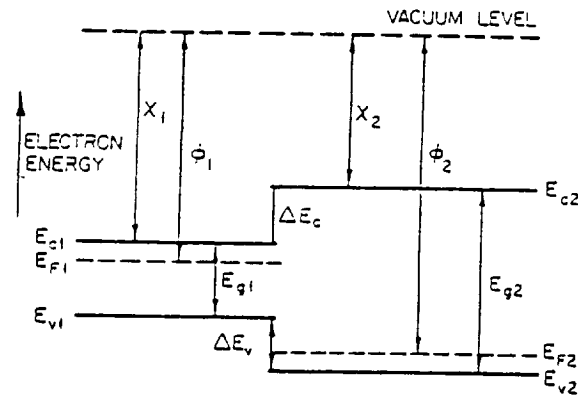


Figure A1
Energy Band Diagram for Two Isolated Semiconductors

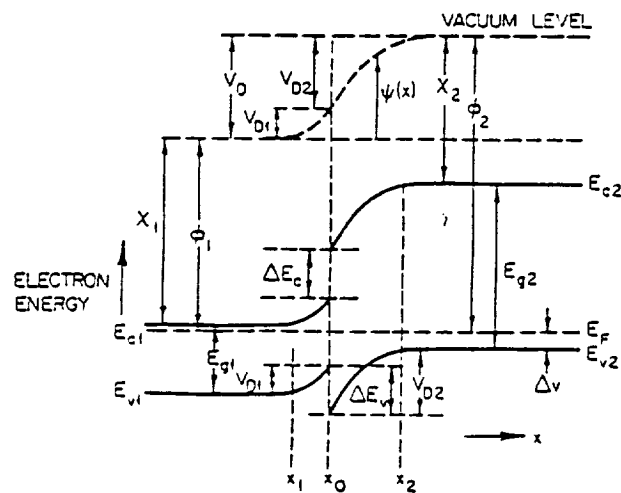


Figure A2
Energy Band Diagram for n-p Heterojunction ($V = 0$)

The energy barrier of a junction for non degenerate materials, materials whose electron affinity and bandgap are not affected by doping, can be calculated using the equation:

$$E_b = E_{g1} + \Delta E_v - \delta_n - \delta_p - qK_2V_a \quad \text{Eq. 1-1}$$

Where:

- E_{g1} = Bandgap of Material One
- ΔE_v = Difference In the Energy of the Valance Bands
- δ_n = Difference Between the Fermi Level and the Conduction Band
- δ_p = Difference Between the Fermi Level and the Valence Band
- q = Charge on an Electron ($1.6 \times 10^{-19}\text{C}$)
- V_a = Applied Voltage

The expression for K_2 is for low forward bias conditions and neglects the effects of injection carriers:

$$K_2 = \frac{1}{1 + N_{D2}\epsilon_2/N_{D1}\epsilon_1} \quad \text{Eq. 1-2}$$

Where:

- N_{D2} = Number of Donor Atoms in Material Two
- N_{D1} = Number of Donor Atoms in Material One
- ϵ_1 = Permeativity of Material One
- ϵ_2 = Permeativity of Material Two

The built-in voltage of the junction, V_D , is the sum of the partial built-in voltages, $V_{D1} + V_{D2}$, where V_{D1} and V_{D2} are the electrostatic potentials of the semiconductors 1 and 2 at equilibrium. The equation for the length of the transition or depletion region of an n-p junction can be found using the derivation:

$$(X_0 - X_1) = \left[\frac{2}{q} \frac{N_{A2}\epsilon_1\epsilon_2(V_D - V_a)}{N_{D1}(\epsilon_1N_{D1} + \epsilon_2N_{A2})} \right]^{1/2} \quad \text{Eq. 1-3}$$

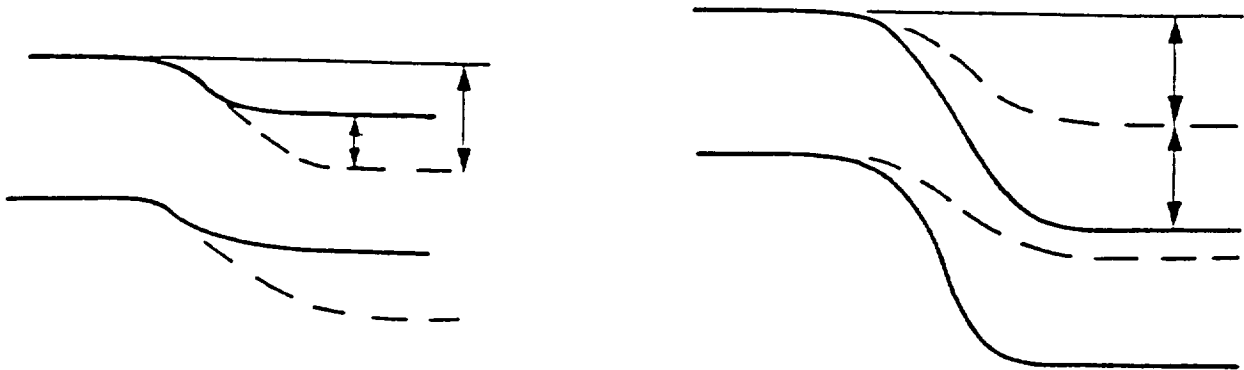
$$(X_2 - X_0) = \left[\frac{2}{q} \frac{N_{D1}\epsilon_1\epsilon_2(V_D - V_a)}{N_{A2}(\epsilon_1N_{D1} + \epsilon_2N_{A2})} \right]^{1/2} \quad \text{Eq. 1-4}$$

The total width of the depletion region is therefore equal to:

$$W = (X_2 - X_0) + (X_0 - X_1) = \left[\frac{2\epsilon_1\epsilon_2(V_D - V_a)(N_{A2} + N_{D1})^2}{q(\epsilon_1N_{D1} + \epsilon_2N_{A2})N_{D1}N_{A2}} \right]^{1/2} \quad \text{Eq. 1-5}$$

Where:

N_{A2} = Number of Acceptor Atoms in Material Two
 V_D = Built-In Voltage



Energy Diagram of a p-n Junction for (a)Forward Bias (b)Reverse Bias

The above diagrams demonstrate the principle of rectification, which states that the total current flowing for a voltage V_a is not the same for a voltage of $-V_a$. The total current flowing left to right through the junction using the equation:

$$I = I_0[\exp(qV_a / \eta kT) - 1] \quad \text{Eq. 1-6}$$

Where:

I_0 = Reverse Saturation Current
 η = Quality Factor
 k = Boltzman's Constant (1.38×10^{-23} J/K)
 T = Temperature (K)

Dividing by the area of the junction the current density can be calculated.

$$J = J_0[\exp(qV_a / \eta kT) - 1] \quad \text{Eq. 1-7}$$

APPENDIX

COMPARISON BETWEEN Si, GaAs, β -SiC AND DIAMOND (300 K)

	Si	GaAs	β -SiC	Diamond
Bandgap (eV)	1.12 (indirect)	1.42 (direct)	2.35 (indirect)	5.48 (indirect)
Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$) μ_e μ_n	1500 450	8500 400	900 50	1800 1600
Electron Sat Drift Vel' V_{sat} (cm s^{-1})	1.0×10^7	2×10^7	2.5×10^7	2.7×10^7
Breakdown Field E_B (V cm^{-1})	3×10^5	4×10^5	4×10^6	1×10^7
Dielectric Constant ϵ	11.9	12.9	9.7	5.6
Thermal Conductivity (K) ($\text{W cm}^{-1} \text{K}^{-1}$)	1.5	0.5	5	20
Johnson Fig. of Merit ¹ $M_J = \left(\frac{E_B V_{\text{sat}}}{2 \pi} \right)^2$ (V s^{-1}) ²	2.3×10^{23}	16.2×10^{23}	2533×10^{23}	18463×10^{23}
Ratio Relative to Silicon	1	7.0	1101	8028
Keys Fig. of Merit ² $M_K = K \left(\frac{V_{\text{sat}}}{\epsilon} \right)^{1/2}$ ($\text{W cm}^{-1/2} \text{s}^{-1/2}$) (K^{-1})	13.8×10^2	6.2×10^2	80.3×10^2	439.2×10^2
Ratio Relative to Silicon	1	0.45	5.8	31.8

¹ Related to the power and frequency limits of transistors

² Describes high frequency limits set by thermal problems